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# The quantitative analysis of magnetic and magneto-optical properties in praseodymium trifluoride

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**Abstract.** This paper first considers the effects of  $L$ - $S$  interaction and the crystal field on both the  $4f$  ground state and the  $5d$  excited state of  $\text{Pr}^{3+}$  ions in the paramagnetic material  $\text{PrF}_3$ , and further takes account of the splitting of the crystal-field ground levels caused by the effective superexchange field  $H_v$  and the applied field  $H_e$ , and then, using the model of double transition with the splitting of the ground state, calculates quantitatively the magnetic susceptibility  $\chi$ , specific Faraday rotation  $\theta_F$ , Verdet constant  $V$ , and their temperature dependence in  $\text{PrF}_3$ . The theoretical calculations show that the magneto-optical effect and its temperature dependence in  $\text{PrF}_3$  are closely related to the superexchange interaction between  $\text{Pr}^{3+}$  ions.  $V^{-1}$  and  $\chi^{-1}$  are linearly dependent of  $T$  in the temperature range of  $110 \text{ K} \leq T \leq 300 \text{ K}$  and independent of  $T$  in the low-temperature regime. The theory is in agreement with the experimental results.

## 1. Introduction

The rare-earth elements in magneto-optical (MO) materials play an important role in the MO effect. A great deal of work, in both experiment and theory, has been done. In 1934, the Van Vleck experiment showed that in paramagnetic rare-earth compounds, the Verdet constant  $V$  exhibits the same temperature dependence as the magnetic susceptibility  $\chi$  [1]. This was proved by the MO theory in paramagnetic materials [2, 3]. However, in 1984, Leycuras and co-workers found that in many rare-earth compounds, the temperature dependence of  $V$  is quite complicated. For  $\text{NdF}_3$  and  $\text{PrF}_3$ ,  $V/\chi$  depends linearly on temperature  $T$ , and in  $\text{CeF}_3$  it depends linearly on  $1/T$  [4]. These phenomena cannot be explained by the previous MO theory.

In our opinion, the shortcoming of the previous theory is that many interactions in paramagnetic materials, in particular the (super)exchange interaction between electron spins, have not been taken into account [5–7]. The (super)exchange interaction can be taken to be equivalent to an effective field  $H_v$ . This field causes the splitting of the ground state together with the applied field  $H_e$ . The electron transitions from all the splitting levels of the ground state ought to have contributions to the MO effect. From this point of view, the complicated temperature dependence of the MO rotation  $\theta$  and the Verdet constant  $V$  have been calculated [8]. It has been shown that Leycuras' work is dependable. In this paper, a quantitative calculation on some main MO properties in the paramagnetic material  $\text{PrF}_3$  has been made. We first consider the effect of the crystal field and the  $L$ - $S$  interaction on both the  $4f$  ground state and the  $5d$  excited state of the  $\text{Pr}^{3+}$  ion in  $\text{PrF}_3$ , and further take account of the splitting of the ground state in the crystal field caused by both  $H_v$  and  $H_e$ , and then, using the model of double transition with the splitting of the ground state, calculate

quantitatively the specific Faraday rotation  $\theta_F$ , Verdet constant  $V$ , magnetic susceptibility  $\chi$  and their temperature dependence in  $\text{PrF}_3$ . The calculations are compared with experiment in detail [4]. The important contribution of the superexchange interaction to the MO effect is pointed out.

## 2. The effect of the $L$ - $S$ interaction on the energy level of the $\text{Pr}^{3+}$ ion

In the paramagnetic crystal  $\text{PrF}_3$ , the Hamiltonian of the  $\text{Pr}^{3+}$  ion is

$$\hat{H} = \hat{H}_0 + \hat{H}_{LS} + \hat{H}_c \quad (1)$$

where  $\hat{H}_0 + \hat{H}_{LS}$  is the Hamiltonian of the free  $\text{Pr}^{3+}$  ion,

$$\hat{H}_{LS} = \zeta(r)\mathbf{L} \cdot \mathbf{S}$$

is the spin-orbital ( $L$ - $S$ ) interaction and  $\hat{H}_c$  is the crystal field. In rare-earth compounds,  $\hat{H}_{LS} > \hat{H}_c$ , so the  $L$ - $S$  interaction must be taken into account first. According to perturbation theory, the energy splitting and its wavefunction under the  $L$ - $S$  interaction can be calculated from the following secular equation:

$$\|\langle \psi(L, M'_L, S, M'_S) | \hat{H}_{LS} | \psi(L, M_L, S, M_S) \rangle - \delta_{M_L M'_L} \delta_{M_S M'_S} (E - E_{nl}) \| = 0. \quad (2)$$

There are two electrons in the 4f level of the  $\text{Pr}^{3+}$  ion; the lowest ground state obtained by  $\hat{H}_{LS} \psi(L, M_L, S, M_S)$  is  ${}^3\text{H}_4$  whose wavefunctions can be expressed as  $|M_j\rangle$  ( $M_j = 4, 3, 2, \dots, -3, -4$ ). In the same way, the lowest excited state with one 4f and one 5d electron is also  ${}^3\text{H}_4$  in form, and correspondingly its wavefunctions are expressed as  $|M'_j\rangle$  ( $M'_j = 4, 3, 2, \dots, -3, -4$ ).

## 3. The energy levels and wavefunctions of the $\text{Pr}^{3+}$ ion in the crystal field

The crystal-field Hamiltonian of one electron of the  $\text{Pr}^{3+}$  ion in  $\text{PrF}_3$  is

$$\hat{H}_c = \sum_{k=0}^{\infty} \sum_{m=-k}^k B_{k,m} Y_{k,m}(\theta, \phi) \quad (3)$$

where the crystal-field parameter  $B_{k,m}$  is

$$B_{k,m} = \frac{4\pi e r^k}{2k+1} \sum_j \frac{q_j}{R_j^{k+1}} Y_{km}^*(\theta_j, \phi_j) = A_{k,m} r^k \quad (4)$$

where the researched  $\text{Pr}^{3+}$  ion is at the zero coordinate, the coordinates of the electron and the  $j$ th neighbouring  $\text{Pr}^{3+}$  ion are  $(r, \theta, \phi)$  and  $(r_j, \theta_j, \phi_j)$ , respectively,  $q_j$  is the electric charge of the  $j$ th neighbouring ion, and  $Y_{k,m}(\theta, \phi)$  is the spherical harmonic function. In real crystals, because of parity and symmetry restrictions, only some terms of the spherical harmonic functions are non-zero. The crystal field in  $\text{PrF}_3$  has approximately the symmetry of  $\text{C}_{3h}$  and so, for 4f and 5d electrons,  $\hat{H}_c$  can be expressed as

$$\hat{H}_{c,4f} = B_{0,0}Y_{0,0} + B_{2,0}Y_{2,0} + B_{4,0}Y_{4,0} + B_{6,0}Y_{6,0} + B_{6,6}Y_{6,6} + B_{6,-6}Y_{6,-6} \quad (5)$$

$$\hat{H}_{c,5d} = B_{0,0}Y_{0,0} + B_{2,0}Y_{2,0} + B_{4,0}Y_{4,0}. \quad (6)$$

Both electrons in the 4f level of the Pr<sup>3+</sup> ion must be taken into account,  $\hat{H}_c = \hat{H}_{c1} + \hat{H}_{c2}$ , where the subscripts 1 and 2 refer to different electrons. Taking  $\hat{H}_c$  as the perturbation, the splittings of the 4f and 5d levels and their eigenfunctions can be calculated from the following secular equation:

$$\| \langle \psi_i | \hat{H}_c | \psi_j \rangle - E^{(0)} \delta_{ij} \| = 0 \quad (7)$$

where  $|\psi_i\rangle, |\psi_j\rangle$  are the eigenfunctions of  $\hat{H}_0 + \hat{H}_{LS}$ , and  $E^{(0)} = E_a^{(0)}$  is the shift of the ground level caused by the crystal field.  $E^{(0)} = E_b^{(0)}$  is the shift of the excited level resulting from the crystal field, and thus the energy of the excited state in the crystal field is  $E_b^{(0)} = E_b^{(0)} + 63\,580 \text{ cm}^{-1}$  [12].

Before we solve (7),  $B_{k,m}$  in  $\hat{H}_c$  must be calculated.  $A_{k,m}$  may be calculated using the point-charge model, and the values of  $\langle r^k \rangle$  can be found in [9]. After the contributions of 39 neighbouring F<sup>-</sup> ions and the other 12 Pr<sup>3+</sup> ions are taken into account, the calculated crystal-field parameters are shown in table 1. The energy levels and the wavefunctions of the 4f and 5d states of the Pr<sup>3+</sup> ion in PrF<sub>3</sub> are shown in tables 2 and 3. Since (6) does not contain a spherical harmonic function  $Y_{k,m}$  with  $m \neq 0$ , there is no mixing of states with different values of  $M_j$  in table 3.

Table 1. The crystal-field parameters of Pr<sup>3+</sup> in PrF<sub>3</sub> (units: cm<sup>-1</sup>).

	$B_{2,0}$	$B_{4,0}$	$B_{6,0}$	$B_{6,\pm 6}$
4f	1262.1	878.8	196.5	-194.0
5d	8025	25 040	—	—

Table 2. The energy levels and the wavefunctions of the ground state <sup>3</sup>H<sub>4</sub> of the Pr<sup>3+</sup> ion in PrF<sub>3</sub> (units: cm<sup>-1</sup>).

$a$	$E_a^{(0)}$	$\psi_a$
1	-288.9	-0.9987 4⟩ - 0.0515 -2⟩
2	-288.9	-0.0515 2⟩ + 0.9987 -4⟩
3	-17.7	-0.7071 3⟩ - 0.7071 -3⟩
4	40.0	-0.7071 3⟩ + 0.7071 -3⟩
5	61.0	0⟩
6	106.3	-0.9486 1⟩ + 0.3164 -1⟩
7	106.3	-0.3164 1⟩ + 0.9486 -1⟩
8	134.2	-0.9987 2⟩ + 0.0515 -4⟩
9	134.2	-0.0515 4⟩ + 0.9987 -2⟩

#### 4. The effect of the effective field on the ground level

The magnetic susceptibility  $\chi$  in PrF<sub>3</sub> conforms to the Curie-Weiss law [4] in the temperature range  $T > 110 \text{ K}$ :

$$\chi = \frac{c}{T - \theta_p} \quad (8)$$

**Table 3.** The energy levels and the wavefunctions of the excited state  $^3H_4$  of the  $Pr^{3+}$  ion in  $PrF_3$  (units:  $cm^{-1}$ ). (We take the energy of the ground state  $^3H_4$  of the  $Pr^{3+}$  ion without the crystal field to be zero.)

$b$	$E_b^{(0)}$	$\psi_b$
1	-827.1	$ 4\rangle$
2	-1400.0	$ 3\rangle$
3	-187.6	$ 2\rangle$
4	1362.8	$ 1\rangle$
5	1964.3	$ 0\rangle$
6	1362.8	$ -1\rangle$
7	-187.6	$ -2\rangle$
8	-1400.0	$ -3\rangle$
9	-827.1	$ -4\rangle$

This signifies that there is a superexchange interaction between the spins of the  $Pr^{3+}$  ions. The superexchange interaction can be equivalent to an effective field [11]

$$H_v = \nu M = \nu \chi H_c \quad (9)$$

where  $M$  is the magnetization, and the coefficient  $\nu = \theta_p/c$ . Equation (8) can be written in another form:

$$\chi^{-1} = \frac{H_i}{M} - \nu. \quad (10)$$

Here the effective field

$$H_i = H_c + H_v.$$

$H_i/M$  is the reciprocal of the susceptibility  $\chi_p$ , which obeys the Curie law in form. According to the quantum theory of paramagnetism, we have

$$\chi_p = \frac{N}{kT} \sum_a |\langle \psi_a | (L_z + 2S_z) \mu_B | \psi_a \rangle|^2 \frac{\exp(-E_a^{(0)}/kT)}{\sum_a \exp(-E_a^{(0)}/kT)}. \quad (11)$$

The fraction on the right-hand side of the equation is the probability of finding an electron in the ground state  $a$ .

From tables 2 and 3 we see that most of the 4f and all the 5d levels are doublet. Under the effect of the effective field  $H_i$ , these degenerate levels will be split again. Because the splitting is much smaller than that caused by the crystal field, a wavefunction which corresponds with a crystal-field level may be used as a base function to calculate the splitting of the level caused by  $H_i$ .

As the superexchange interaction is related to the spin  $\hat{S}$ , in neglecting the anisotropy of the superexchange interaction the perturbation Hamiltonian is

$$\hat{H}_i = \mu_B H_c (\hat{L}_z + 2\hat{S}_z) + \mu_B H_v 2\hat{S}_z = \mu_B H_c [(\hat{L}_z + 2\hat{S}_z) + 2\nu \chi \hat{S}_z]. \quad (12)$$

According to degenerate perturbation theory, the splitting of the 4f levels of the  $Pr^{3+}$  ion caused by  $H_i$  can be found from the secular equation

$$\| \langle \psi_a | \hat{H}_i | \psi_{a'} \rangle - E_a^{(1)} \delta_{aa'} \| = 0 \quad (13)$$

where  $|\psi_a\rangle$  and  $|\psi_{a'}\rangle$  are the degenerate wavefunctions of the same crystal-field level in table 2. In the first approximation, the shift of the ground level of the Pr<sup>3+</sup> ion resulting from  $H_i$  is given by

$$E_a^{(1)} = \mu_B H_c [\langle \psi_a | \hat{L}_z + 2\hat{S}_z | \psi_a \rangle + 2\nu\chi \langle \psi_a | \hat{S}_z | \psi_a \rangle] \quad (14)$$

where  $|\psi_a\rangle$  is the wavefunction of each 4f level in table 2. The energy shift of each 4f level under the effect of  $H_i$  is shown in table 4.

At room temperature,  $kT \simeq 200 \text{ cm}^{-1}$ . Obviously, there are certain electron distribution probabilities for every level in table 4. When we calculate  $\theta_F$  and  $V$ , all these levels must be taken into consideration. The energy between the excited-state levels caused by the crystal field is much larger than the splitting of the excited state caused by  $H_i$ , and the splitting of the excited state resulting from the superexchange interaction has no contribution to the MO effect [10], so the influence of  $H_i$  on the levels and the wavefunctions of the excited state can be neglected.

Table 4. The energy shifts of the ground state <sup>3</sup>H<sub>4</sub> under the effect of  $H_i$ .

$a$	$E_a^{(1)} (\text{cm}^{-1})$
1	$\mu_B H_c (3.1873 - 1.5936\nu\chi)$
2	$\mu_B H_c (-3.1873 + 1.5936\nu\chi)$
3	0
4	0
5	0
6	$\mu_B H_c (0.6398 - 0.3199\nu\chi)$
7	$\mu_B H_c (-0.6398 + 0.3199\nu\chi)$
8	$\mu_B H_c (1.5873 - 0.7936\nu\chi)$
9	$\mu_B H_c (-1.5873 + 0.7936\nu\chi)$

## 5. The specific Faraday rotation $\theta_F$ and the Verdet constant $V$

The MO effect in PrF<sub>3</sub> is caused by 4f–5d electric-dipole transitions in the Pr<sup>3+</sup> ion. Neglecting the linewidth  $\Gamma_{ab}$ ,  $\theta_F$  is given by

$$\theta_F = \frac{m\omega_p^2}{4\hbar e^2 n c} \frac{(n^2 + 2)^2}{9} \sum_{a,b} \frac{\omega^2}{\omega_{ab}^2 - \omega^2} (|P_{ab}^-|^2 - |P_{ab}^+|^2) \beta_a \quad (15)$$

where

$$\omega_p^2 = 4\pi N e^2 / m.$$

$N = 1.912 \times 10^{22} \text{ cm}^{-3}$  is the number of ions per unit volume,  $n = 1.59$  is the average index of refraction,  $\omega$  is the frequency of the incident light, and  $\hbar\omega_{ab}$  is the energy-level separation between the excited state  $b$  and the ground state  $a$ . The matrix elements of the 4f–5d electric-dipole transitions excited by left- and right-handed circularly polarized light are

$$P_{ab}^{\pm} = \langle \psi_a | e(x \pm iy) | \psi_b \rangle = \mp (8\pi/3)^{1/2} e \langle \psi_a | r | \psi_b \rangle \langle \psi_a | Y_{1,\pm 1} | \psi_b \rangle \quad (16)$$

where

$$\langle \psi_a | r | \psi_b \rangle = \langle r \rangle = 2.339a_0$$

( $a_0$  is the Bohr radius), and  $\langle \psi_a | Y_{1,\pm 1} | \psi_b \rangle$  is calculated according to the Wigner-Eckart law. From all 162 matrix elements of the transitions, it can be seen that the probabilities of the electric-dipole transitions excited by left- and right-handed circularly polarized light are equal. From (15), the main reason for the Faraday rotation in  $\text{PrF}_3$  is that the occupation probabilities of an electron in the two split levels of the ground state caused by  $H_i$  are not the same. The probability  $\beta_a$  of an electron lying in the split level  $a$  as shown in table 4 is given as

$$\beta_a = \exp[-(E_a^{(0)} + E_a^{(1)})/kT] \left( \sum_{a=1}^9 \exp(-E_a/kT) \right)^{-1}. \quad (17)$$

Substituting the calculated values of (16) and (17) into (15), and using  $V = \theta_F/H_e$ , we get the values of  $\theta_F$  and  $V$  at different temperatures;  $\hbar\omega_{ab}$  is known from tables 2, 3 and 4. Figures 1 and 2 show the theoretical and experimental curves of  $\chi^{-1}$  against  $T$  and  $V^{-1}$  against  $T$ , respectively [4].

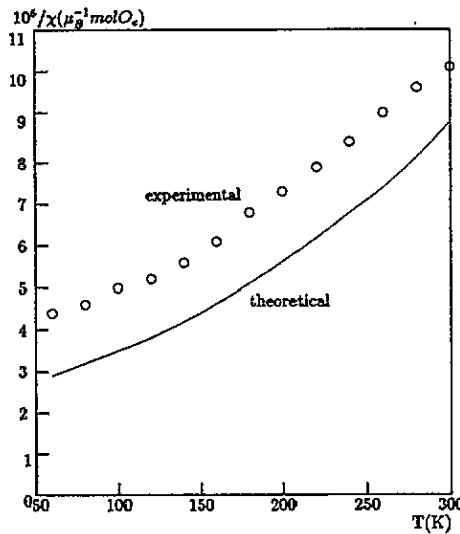


Figure 1. Inverse of the magnetic susceptibility against temperature in  $\text{PrF}_3$ .

## 6. Discussion

The calculations show the following characteristics.

(i) In the temperature region  $\sim 110$ – $300$  K, the reciprocals of the magnetic susceptibility  $\chi^{-1}$  and the Verdet constant  $V^{-1}$  in  $\text{PrF}_3$  are nearly linearly dependent upon  $T$ . When  $T < 110$  K, they are non-linear. This is in good agreement with the experimental results

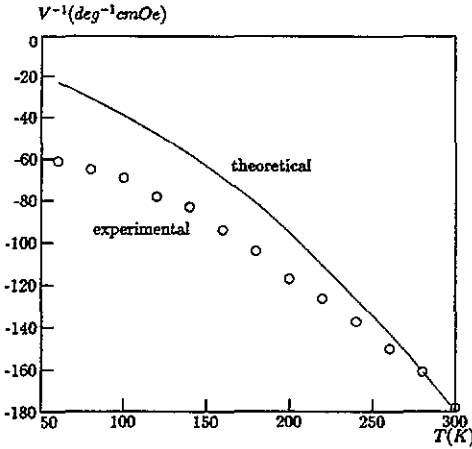


Figure 2. Inverse of the Verdet constant against temperature in  $\text{PrF}_3$  at a wavelength of  $0.6328 \mu\text{m}$ .

of [4]. This non-linear dependence comes from the non-linear dependence on temperature of  $\beta_a$ , which is the probability of finding an electron in the split ground state.

(ii) It can be shown by analysing (16) that the stronger the (super)exchange interaction in paramagnetic materials the larger the probability  $\beta_a$  of an electron staying in the lower split level of the ground state, and  $\theta_F$  and  $V$  increase with  $H_i$  [5]. When the temperature increases, the  $\beta_a$  of an electron staying in the upper split level of the ground state also increases, and the  $\beta_a$  of an electron staying in the lower split level becomes correspondingly smaller. This makes  $\theta_F$  and  $V$  decrease.

(iii) The Leycuras experiments showed that when  $H_e = 20 \text{ kOe}$  and  $T \leq 16 \text{ K}$ ,  $\chi$  is independent of  $T$ . In the same temperature region,  $V$  is also independent of  $T$ . Based on (15) and (17), if  $E_a^{(1)}/kT \rightarrow 1$ ,  $V$  will be independent of  $T$ . This temperature region can be estimated as follows. The split energy of the 4f ground state of the  $\text{Pr}^{3+}$  ion under an applied field  $H_e = 20 \text{ kOe}$  is equal to  $2\mu_B H_e$ . The temperature that makes  $kT \sim 2\mu_B H_e$  is 3 K. Furthermore, taking the effective superexchange field  $H_v$  and the electron-orbit magnetic moment into account, the temperature region which makes  $E_a^{(1)}/kT \rightarrow 1$  is consistent with that obtained from experiment,  $T < 16 \text{ K}$ .

The theoretical values of  $V$  conform quite well to the experimental results; it is again proved that the three-level transition model (i.e. the double-transition model with ground-state splitting) is correct. That is, the split levels of the ground state caused by both the effective (super)exchange field and the applied field ought to have contributions to the MO effect. This also is the internal cause of why the MO effect in some paramagnetic materials has a complicated temperature dependence.

(iv) For  $\text{PrF}_3$ , raising the density of the  $\text{Pr}^{3+}$  ions can not only increase the value of  $\omega_p^2$  but can also enhance the superexchange interaction between  $\text{Pr}^{3+}$  ions. Thus, raising the density of  $\text{Pr}^{3+}$  ions suitably is a valid way of strengthening the MO effect.

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**References**

- [1] Van Vleck J H and Hebb M H 1934 *Phys. Rev.* **16** 17
- [2] Shen Y R 1964 *Phys. Rev.* **133** A511
- [3] Freiser M J 1968 *IEEE Trans. Magn.* **MAG-4** 152
- [4] Leycuras C, Le Gall H, Guillet M and Marchard A 1984 *J. Appl. Phys.* **55** 2161
- [5] Davis J A and Bunch R M 1984 *Appl. Opt.* **23** 633
- [6] Suits J C 1972 *IEEE Trans. Magn.* **MAG-8** 95
- [7] Bennett H S and Stern E A 1965 *Phys. Rev.* **137** A488
- [8] Liu Gong-qiang, Huang Yanping and Yu Zhiqiang 1990 *Phys. Rev. B* **41** 749
- [9] Starostin N V 1976 *Crystal Spectroscopy* (Moscow: Nauka) p 12
- [10] Crossley W A and Cooper R W 1969 *Phys. Rev.* **181** 896
- [11] Condon E U and Shortley G H 1951 *The Theory of Atomic Spectra* (Cambridge: Cambridge University Press)
- [12] Sugar J 1965 *J. Opt. Am.* **55** 1058